Global scale evidence for the refractory nature of riverine black carbon

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ABSTRACT

Wildfires and fossil fuel combustion release large amounts of greenhouse gases into the atmosphere, but also produce Black Carbon (BC, or pyrogenic carbon) from incomplete combustion. Processes controlling BC production and its fate are an integral component of the carbon cycle. Constraining BC export from land to the ocean is critical given on-going changes in land use and climate that affect fire occurrence and BC dynamics. Here, we compile an inventory of concentration and radiocarbon contents ($\Delta^{14}C$) of particulate BC (PBC) for a globally distributed suite of rivers, and show that PBC fluxes co-vary with river sediment particulate organic carbon (POC), indicating that PBC export is primarily controlled by erosion. River PBC is not exclusively from modern sources but includes PBC that has aged (up to 17,000±780 ^{14}C yrs) from intermediate terrestrial carbon pools in several high latitude rivers. The global, flux-weighted ^{14}C age of PBC delivered to the ocean (3,700±400 ^{14}C yrs, $\Delta^{14}C$ = -372±28‰) implies protracted storage in terrestrial reservoirs before export. River PBC accounts for 15.8±0.9% of POC, amounting to a global river PBC flux of 0.017-0.037 Pg yr^{-1} to the oceans. This corresponds to 4-32% of the of global annual BC production, implying an export efficiency that is one to two orders of magnitude greater than for POC. When buried in marine sediments, PBC is sequestered, forming an important long-term sink for atmospheric CO_2.

Forest fires and fossil fuel combustion release large amounts of carbon as greenhouse gases and aerosols into the atmosphere, contributing to the on-going changes in Earth's climate that are occurring at an unprecedented rate [1]. Up to 27% of this fire-derived carbon is transformed into Black Carbon (BC, or pyrogenic carbon, charcoal

residues [2]) – a byproduct of incomplete combustion - rather than emitted as greenhouse gases [3]. The majority of BC is from vegetation fires (Figure 1). Once incorporated into surface reservoirs (e.g. soils, lake sediments), BC participates in many biogeochemical processes, and influences carbon cycling on local to global scales [3,4]. Biomass burning transfers carbon from fast-cycling (atmosphere-biosphere) pools to more slowly cycling soil and sedimentary reservoirs [5], creating a long-term carbon sink [6,7]. Due to its aromatic structure, a substantial fraction of BC decomposes slowly [8,9], and can persist in soils for hundreds to thousands of years [5,10].

Greater understanding of the role of this slow-cycling component of the carbon cycle and its significance as a sink of atmospheric CO_2 requires improved constraints on the origin, dynamics and fate of BC. River systems connect terrestrial and marine carbon cycles, exporting approximately 2.7 Pg C yr^{-1} to the oceans [11], where it is ultimately either mineralized to CO_2 and CH_4 [12-14] or sequestered in sediments [15]. Rivers deliver BC from land to the ocean both as particulate BC (PBC) in particulate organic carbon (1<63 µm) and dissolved BC (DBC) in dissolved organic carbon (<1 µm)[4,16]. Dissolved BC, which comprises a substantial fraction (10%) of dissolved organic carbon (OC) globally, is continuously exported from soils for decades after wildfire burning [17,18] (26.5 Tg yr^{-1}), and can cycle in the deep ocean on millennial timescales (~ 20,000 ^{14}C yrs) [19,20]. The global amount and age of PBC transported by rivers, has remained largely unknown until now. PBC river fluxes, age and transport is essential for constraining land-ocean transfer as well as assessing its significance as a CO_2 sink by sequestration in continental margin sediments [21]. Current global PBC flux estimates vary by a factor of 20 (0.005-0.108 Pg yr^{-1}) [22,23], and the magnitude and timescales of transport, transformation and degradation processes are not well understood [16,24]. As

river basins are facing anthropogenic pressures, both directly via changes to the land surface (e.g. increasing fire intensity and frequency, accelerated deforestation, conversion to agriculture) and fluvial networks (e.g. dams, channelization, irrigation), and indirectly via climate change (e.g. increasing temperatures and an invigorated hydrological cycle) [11,25,26], we need to constrain PBC river export to assessing past and future perturbations of this slowly cycling pool in the carbon cycle.

Here, we use the abundance and radiocarbon (^{14}C) content to constrain the flux and age of river PBC of 18 globally distributed rivers. We quantify river PBC in suspended or deposited sediments collected at the terminus of 11 of the largest rivers worldwide, (such as the Amazon, Congo, Brahmaputra, and major Arctic rivers) and 7 small mountainous rivers [27] (S.Table 1). These samples represent 15-34% of the global organic carbon exported by rivers (high and low estimates of export from [28]). We used river suspended sediments (collected by filtration) or freshly deposited river sediments (<63 µm) (Supplementary Materials, S.Figure 1). We measured BC in Particulate Organic Carbon (POC, as <63um size fraction), providing the age of PBC at or near the river terminus (S.Table 1, S.Figure 1). To characterize PBC derived predominantly from residues of biomass burning, we use chemical oxidation to liberate corresponding benzene polycarboxylic acids (BPCAs) [29]. The analytical window captured by this method implies that the mass weighted PBC fluxes are conservative under-estimates for PBC fluxes, since it does not include by-products of low-temperature fires (e.g. levoglucosan [21,30] We assume BC molecular markers have the same ^{14}C age within BC. Subsequently, we purified BPCA marker compounds [29] and converted them to CO_2 followed by ^{14}C measurement by gas ion source Accelerator Mass Spectrometry [31]. PBC fluxes from each river were estimated by multiplying the relative PBC

concentration (from BPCA concentrations) with the reported biospheric OC yield of each river given by Galy et al. [28], thereby normalizing PBC to biospheric OC export. The biospheric OC yield was calculated using previous reported data and linear correlations between biospheric OC yield and sediment yield in Galy et al., [28] (Supplementary Information).

BC as a major component of riverine particulate organic carbon

We find PBC comprises a significant component of river biospheric POC (15.8±0.9% PBC river flux-weighted mean, n=18, Supplementary Materials). This proportion of river PBC is similar to global averages of the riverine dissolved BC (10.6±0.7%) [18] and of soil organic carbon (13.7%) [32]. The proportion of PBC as a component of river POC ranges from 2.7±0.4 % PBC (Pettaquamscutt) to 32.9±2.9 % PBC (Eel) (Supplementary Materials, S.Table 2, S.Figure 2). Corresponding PBC fluxes from rivers range from 8±2 (Fraser) to 1162±218 Gg yr^{-1} (Amazon). There is no correlation between BC concentration and river basin drainage size (S.Figure 3), however PBC yield is positively correlated with suspended sediment yield (sediment discharge normalized to the drainage area). This correlation follows a power-law relationship (r^2=0.61) (Figure 3a) and indicates that the rate of PBC export is controlled primarily through soil erosion, mobilization and transport processes, much like export of POC [28,33]. PBC concentrations vary by a half order of magnitude, while suspended sediment yield varies by four orders of magnitude, illustrating that PBC export is primarily controlled by erosion (not concentration). Given that rivers sequester the majority of terrestrial exported POC by burial in ocean sediments [34], these observations establish a direct link between soil erosion and PBC sequestration on continental margins.

Time-lags between production and riverine export of PBC

We find a large range in PBC $\Delta^{14}C$ values, indicating fast (+74±62 ‰, modern, Congo) to slow (-880±12‰, 17,000±780 ^{14}C yrs, Colville) PBC cycling within individual watersheds (Figure 3, S. Table 1). The global flux-weighted age average of 3,700±400 ^{14}C yrs (-372±28‰) is significantly higher (older) than the few measurements on river dissolved BC (450±280 ^{14}C yrs, 475±150 ^{14}C yrs and 1140 ^{14}C yrs, from [16,19,20]). Globally, PBC is older than total POC, with two exceptions in the Godavari and Congo Rivers where PBC is modern (Figure 3). Assuming all BC produced from burning of modern biomass has a mean post-bomb $\Delta^{14}C$ value of +100‰ and BC derived from fossil fuel combustion has a $\Delta^{14}C$ value of -1000‰ (i.e., is radiocarbon-depleted), we estimate that 44±28% of river PBC is from fossil fuel contributions (Supplementary Materials). However, assuming only two end members is overly simplistic given the range of potential PBC sources and transport pathways [16,35]. A regional study in the Pettaquamscutt River basin (USA) estimated a maximum fossil fuel BC contribution of only 19%, and indicated that there is a time lag between production and river export of PBC[35]. This implies that BC can "pre-age" during temporary storage in intermediate terrestrial reservoirs (e.g. soils) [35].

River PBC thus reflects at least three pools: i) biomass-derived char from recent vegetation fires, ii) pre-aged BC (held within the catchment in soils, wetlands and floodplains before river transport and ocean deposition [35]), and iii) fossil fuel-derived BC. Fossil fuel-derived BC mass contributions are considered minor for the following reasons. First, the annual production of biomass-derived BC (114-383 Tg yr^{-1}) is one to two orders of magnitude higher than BC produced by fossil fuel combustion (2-29

Tg yr^{-1}) (Figure 1). Second, soil formation rates span centuries to millennia, and the vast majority of BC eroded from soils must pre-date the beginning of the industrial revolution. Third, there is mounting evidence that soil OC inputs dominate the POC load in most river systems [28,36], as indicated for PBC by our own data. PBC contributions to river PBC pools are therefore likely dominated by inputs from biomass burning.

Given the importance of soil OC as a component of riverine POC export, rivers constitute a source of pre-aged PBC. PBC can be temporarily stored in soils and alluvial deposits for thousands of years [37,38], much like other molecular markers of terrestrial vegetation (e.g., higher plant-derived long-chain *n*-alkanes and *n*-alkanoic acids) [39-41]. River PBC ^{14}C ages are generally older than those of other terrestrial vegetation molecular markers [39-41] implying slower PBC turnover rates. Moreover, the correlation between $\Delta^{14}C$ values of PBC and POC (Figure 3b, r^2=0.48, p=0.005) suggests that pre-aged soil OC, including PBC, is an important component of overall OC export. This linear relationship is close to unity (1.05±0.02), indicating that common mechanisms are responsible for aging of both soil OC and BC pools, as well as implying that the ratio of BC and non-BC reactivity is roughly constant, regardless of environmental conditions. PBC experiences pre-aging (relative to POC) in river basins by a relatively constant amount globally, including locations where environmental conditions both favor preservation or mineralization.

Global implications and future outlook

Although sequestration in marine sediments is considered to be the ultimate fate of BC [21] (Figure 1), marine sediment BC burial fluxes only account for 3-10% of global

BC production fluxes [42]. In soils, BC constitutes on average 13.7% (ranging to 50%) of total organic carbon [32]. This inconsistency between BC in soils and marine sediments raises the question as to where the majority of BC produced annually on land goes. Inland waters are both significant holding pools of organic carbon (with storage of up to 50% of carbon along the river-to-ocean continuum), and processers of this carbon [12,14,43]. In this way, PBC may be sequestered for years up to millennia in intermediate reservoirs prior to export and burial in marine sediments [35,44]. For example, PBC has been found to be retained in alluvial deposits for thousands of years [37], implying that BC can undergo pre-aging en-route to its ultimate burial site. The large fluxes and diverse ages of PBC in our study supports the conclusion that dissolved and particulate BC pools in rivers are partially decoupled, with dissolved BC driven by hydrology [16,19,45] whereas PBC is subject to erosional and depositional dynamics (Figure 1). This preliminary global assessment of river PBC flux represents an underestimate since it is based on BPCA markers tracing the most refractory components of BC (i.e., it does not include more labile BC from low temperature fires [30]). Our study highlights the need for further source-to-sink studies to determine controls on the fluxes and degrees of pre-aging of PBC in river catchments prior to export.

Assuming a soil BC stock of 200 Pg [32], and a BC production rate of 0.123-0.56 Pg C per yr , the BC mean turnover time in soils at steady state ranges from 1600 to 3500 yrs (Figure 3) [4]. This is much longer than estimates of bulk soil OC turnover times (mean residence time, 25-110 yrs) [46], highlighting the refractory nature of BC, and consistent with our estimated watershed-wide erosion rates. Using our weighted mean PBC as a fraction of biospheric POC (15.8±0.9%) and estimated global biospheric

POC flux (0.157^{+74}_{-50} Pg yr^{-1} [28]), we estimate an annual global flux of PBC to the ocean of 0.017-0.037 Pg BC. This riverine PBC flux is approximately equal to the global dissolved BC flux (0.027 Pg yr^{-1})[18] indicating that, relative to atmospheric fluxes (0.002-0.005 Pg yr^{-1})[4], river transport serves as the dominant process for mobilization of BC from land to ocean (Figure 1). Thus, rivers transport 4-32% of the 0.114-0.383 Pg BC that is produced annually to the oceans. This is one to two orders of magnitude larger than the fraction of biospheric OC that is exported, indicating that a much larger fraction of PBC (relative to biospheric OC or dissolved BC) is laterally exported instead of respired in soils. Furthermore, the average age of riverine PBC (3,700±400 ^{14}C yrs) is closer to the calculated mean BC turnover time (800-1000 yrs) [47] in soils than that of the biospheric OC (~50 yrs)[48]. Together these observations provide global evidence that PBC is more refractory than POC. Like POC [49], river PBC is likely to be transferred and buried in marine sediments on continental margins, and thus preserved over geological timescales. Indeed, our estimated global riverine PBC flux amounts to 20% of the terrestrial organic carbon stored annually in ocean sediments [50], suggesting that processes of BC production, protracted storage in terrestrial reservoirs, mobilization and burial in marine sediments thus represent an important geologic atmospheric CO_2 sink.

These findings have implications for our understanding of the role of BC cycling in the face of direct (e.g., land-use) and indirect (climate) anthropogenically-driven change. Some increases in the intensity and frequency of fires with on-going climate change [51,52] may enhance BC production. Here, we find river PBC is efficiently exported and stored in sediments rather than degraded to CO_2 en-route to burial in the ocean, suggesting a negative feedback to increased biomass burning. Such interpretations

are likely overly simplistic, by not taking into account seasonal differences between production and erosion of BC. However, the strong correlations imply that these trends are robust at a global scale. Nevertheless, it is clear that further consideration of BC dynamics within river basins at regional and global scales is warranted in order to better constrain this important component of the carbon cycle.

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All authors contributed scientific comments and input on this manuscript. T.E., M.S, D.W. and A.C. contributed to the design of the study. A.C. and D.W. measured the samples for BC content and radiocarbon values. U.H., N.H. and L.W. provided analytical assistance to the radiocarbon measurement of samples and quality control. V.G., A.C., M.S., E.S. and T.E. contributed to data interpretation. A.C. wrote the paper

and built the figures. Samples and supplementary data were provided by T.E., G.N, M.U., T.B., C.F., E.S., M.Z., B.V., V.G., M.R. and B.P.E.

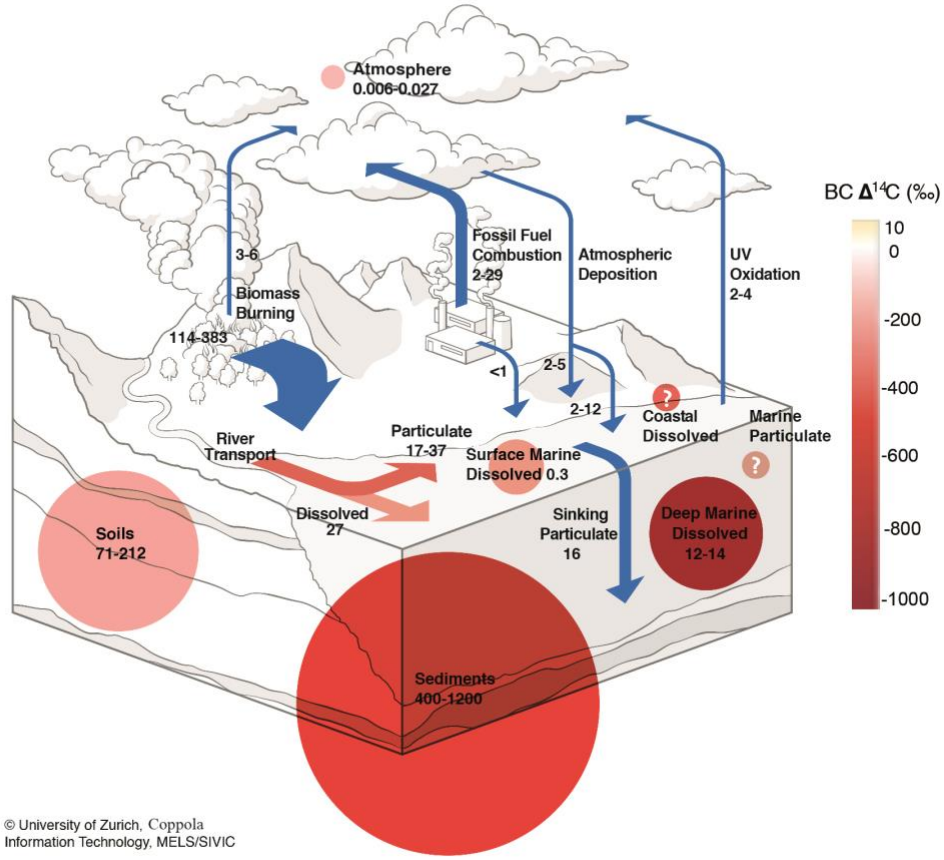


Figure 1. Global schematic synthesis of the BC cycle in major reservoirs. Estimates are derived from Supplementary Table 3. The relative size of the reservoir (Tg) is given by the size of the circle. Schematic BC $\Delta^{14}C$ values are given by the shade of white (modern, post 1950) to dark red (ancient -1000‰) in (circle) reservoirs and river BC (arrow) pools. Fluxes are in Tg yr^{-1} given by the relative size of the blue and red arrows.

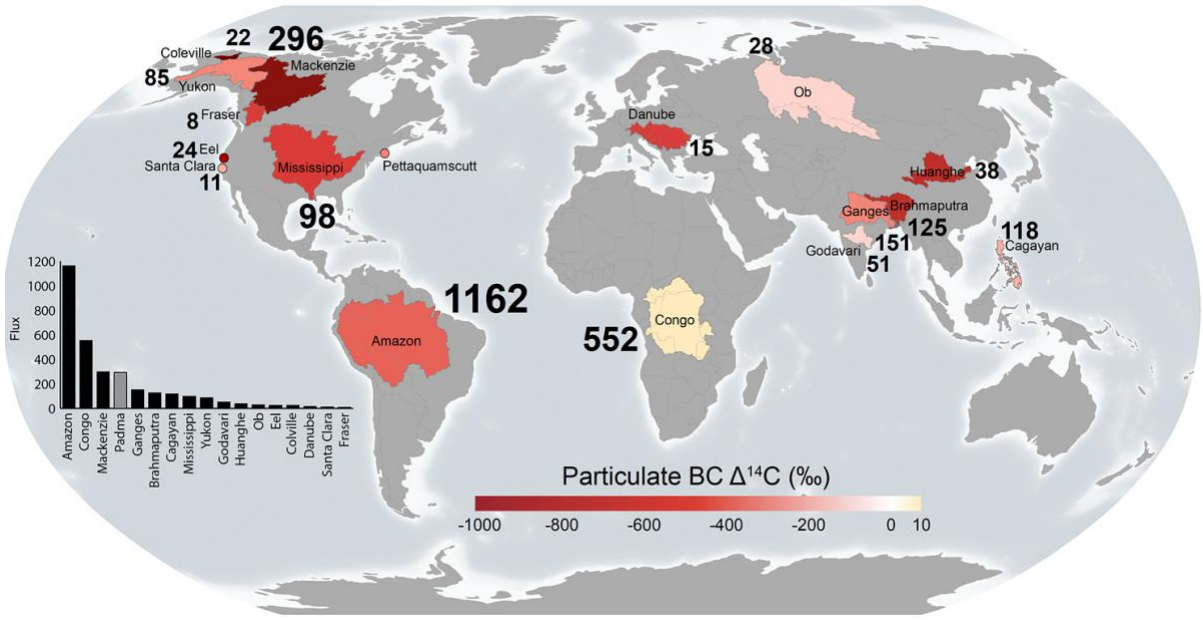
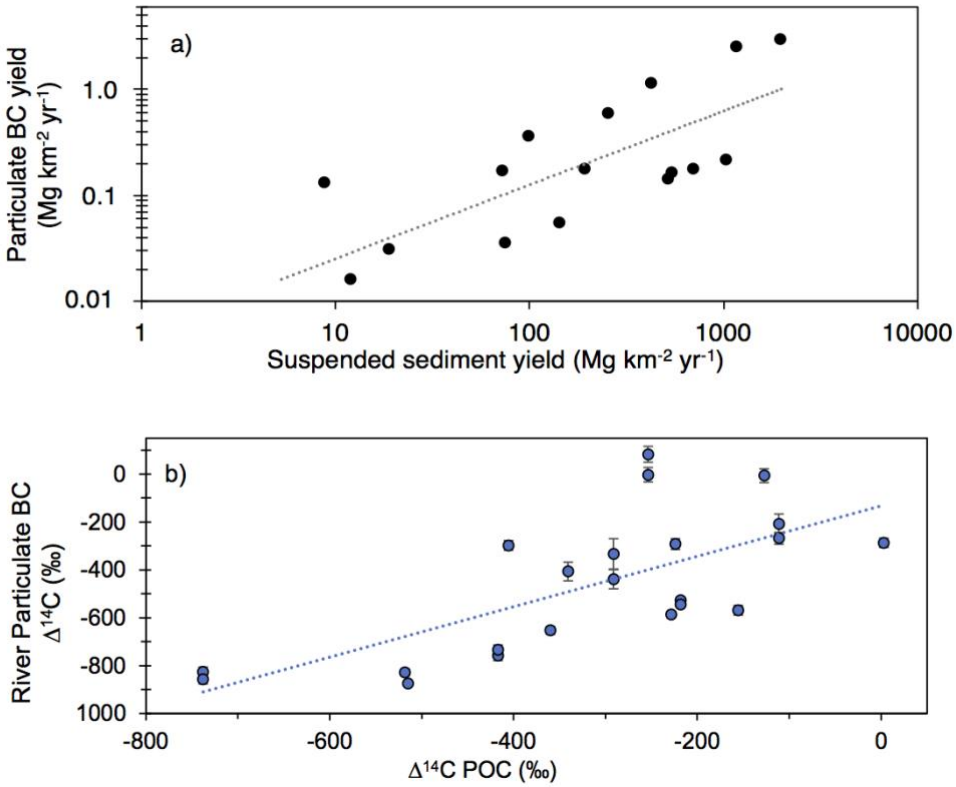


Figure 2. PBC fluxes (values in Gg yr $^{-1}$) and PBC $\Delta^{14}C$ values (in ‰). PBC $\Delta^{14}C$ values are given by the shade of yellow (bomb) to dark red (ancient -1000‰) for the river catchment. Rivers were sampled at their outlets. Small colored circles indicate small mountainous rivers with drainage basin areas less than 250,000 km^2. The histogram represents fluxes per river (Gg yr $^{-1}$), where the grey bar represents the flux of the Padma, which is the combined fluxes of the Brahmaputra and Ganges rivers.



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314 Figure 3. a) Relationship between PBC yield and suspended sediment yield. PBC
315 was normalized to the biospheric OC yield given in [28]. The regression line is $Y_{PBC\ yield}$
316 $=0.005(Y_{sed})^{0.69}$; r^2=0.61; P<0.001. b) Relationship between $\Delta^{14}C$ values of PBC and
317 POC. The regression line is $Y_{PBC14C}=1.05(X_{biosphericOC})-132$; r^2=0.48; P<0.001.

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